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ORIGINAL ARTICLE

Comparative studies of the rheological behaviour of oil epoxy and oil polyesteramide blends with polymethacrylic acid

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Abstract Polymer blends have replaced a variety of pristine polymers in different sectors due to their desired synergetic properties such as durability, heat resistance, reduced wear & tear, flexibility, chemical resistance and longer shelf life that can be achieved by making minor alterations in their compositions. The modification of polymer blends by using sustainable resource based polymers can not only fulfil our ecological but also our economic and social needs. The present work reports the compatibility studies of oil derived epoxy and polyesteramide blends with polymethacrylic acid (PMA). The aim is to highlight the role of rheology in predicting the compatibility of these blends in the solution and solid phases which is a crucial parameter that decides the processibility and viability of these materials for commercialization.

1. Introduction

Polymer blending is a well-known technique used for the modification of desired properties of polymers because it uses conventional technology at low cost (Kaplan, 1998; Gross and Scholz, 2001). Depending on the thermodynamics of the mixed constituents and the ratio of their composition, miscible and immiscible blends can be prepared (Zhang et al., 1996). In miscible blends, both blend components lose part of their identity and the final properties usually are the arithmetical average of both blend components. In heterogeneous blends, the properties of all blend components are present. Weaknesses of one polymer can to a certain extent be camouflaged by strengths of the other (Ke et al., 2003). In certain cases, the properties of the either homogeneous or heterogeneous blend can be better than those of the individual components. This synergism is unfortunately hard to predict. Heterogeneous blends appear in a variety of morphologies. The best known and most frequently observed morphologies are: (i) dispersion of one polymer in the matrix of the other polymer; and (ii) co-continuous two-phase morphology. The type of morphology obtained is dependent on the nature of the blend components, the viscosity and the viscosity ratio of both polymers at the blending temperature, and the blend composition. The overall physical,

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chemical and morphological properties of the polymer blends are therefore governed by the individual properties of the blending constituents (Zhao et al., 2003; Ohkoshi et al., 2000). Hence, a good understanding of the relation between the morphology development and the processing conditions is required to design products with desired properties (Willett and Shogren, 2002).

Polymers from renewable resources have attracted an increasing amount of attention over the last two decades due to environmental concerns, and finite petroleum resources. Renewable resources can provide an interesting sustainable platform to substitute partially, petroleum-based polymers through the design of blends that can exhibit superior properties when compared to the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values (Yu et al., 2004). Plant oils are now being considered as the most important renewable raw materials for the production of bio-based polymer materials (Wollerdorfer, 1998; Herrmann et al., 1998). Plant oils are triglycerides (triesters of glycerol with long-chain fatty acids) with varying composition of fatty acid depending on the plant, the crop, the season, and the growing conditions (Wool et al., 2002). The molecular parameters affecting the physical and chemical properties of plant oils are the stereochemistry of the double bonds of the fatty acid chains, the degree of unsaturation, and the length of fatty acids. However, the degree of unsaturation mostly remains the key-parameter of plant oils. Other types of fatty acid functionalities (e.g., epoxy, hydroxyl, cyclic and furanoid groups) are available as well (Bailey, 1996). In industrial practice, drying oils are most frequently used to form resins due to their high ability for auto-oxidation, peroxide formation, and subsequent radical polymerization, as currently applied in paint and coating formulations (Ahmad et al., 2002; Teng and Soucek, 2000).

The rheology of polymer blends has received a lot of attention because of its technological importance in polymer processing (Blayo et al., 2001). It is often essential to know the viscoelastic behaviour of polymer blends, not only for reaching optimum processing conditions, but also for collecting valuable information on the flow mechanism and its effect on both phase morphology and ultimate mechanical properties (Blayo et al., 2001). Control of the phase morphology during blend processing is a key issue for the production of new materials with improved properties. Hence, rheological properties of polymer blends are strongly influenced by the morphology of these materials which depends on the composition of the constituents. Rheological properties are therefore essential to relate the microstructure, physical, chemical and mechanical properties of polymer blends.

In our earlier investigations we have reported the solution blending of these plant oil derived polymers with existing commercial polymers such as polystyrene (PS), polyvinyl alcohol (PVOH), polymethylmethacrylate (PMMA) and polymethylacrylic (PMA) to obtain sustainable resource based polymer blends showing mechanical properties ranging from elastomers to rigid and tough plastics, depending on the composition and the type of plant oil derived polymer used for the formulation of blends which has been extensively investigated by Ashraf et al. (2005, 2006, 2007a–d).

We have also reported the compatibility and miscibility of the blends of dehydrated castor oil epoxy (DCOE), linseed oil epoxy (LOE) as well as dehydrated castor oil (DCPEA) and linseed oil polyesteramides (LOPEA) blends with PMA (Ashraf et al., 2005, 2006, 2007a–d). The blends with PMA were prepared by mixing the DCOE/LOE and LOPEA/DCPEA with PMA in the weight ratios, 80/20, 60/40, 40/60, and 20/80 to obtain 2 wt.% and 4 wt.% solutions of DCOE/PMA, LOE/PMA, DCPEA/PMAA and LOPEA/PMAA blends in dimethyl sulfoxide. The solution phase studies were carried out in 2% and 4% blend solutions using the techniques of viscosity, ultrasonic velocity and adiabatic compressibility and density measurements. Blends of DCOE with PMAA were found to be semi-compatible in 2% and 4% solutions by ultrasonic velocity, viscosity and density measurements. The films were transparent, flexible and sticky, having poor stiffness. Thermal analysis, as well as morphological investigations, indicated that the blends were incompatible in solid phase. Blends of LOE with PMAA were found to be semi-compatible in 2% and 4% solution by ultrasonic velocity, viscosity, and density measurements (Ashraf et al., 2006).The films were slightly translucent, flexible, and sticky, having poor stiffness. Thermal analysis as well as morphological investigations indicates that the blends are incompatible in solid phase (Ashraf et al., 2006). DCPEA and LOPEA show immiscibility with PMA in solution phase (Ashraf et al., 2007). LOPEA showed higher immiscibility than DCPEA which was confirmed by viscosity and ultrasonic velocity measurements. LOPEA also showed higher immiscibility with PMA in solid phase. In fact, DCPEA showed some miscibility with PMA in solid phase below 40 wt.% PMAA (Ashraf et al., 2007). The films of DCPEA/PMAA blend with 20 wt.% PMA were transparent and highly stiff (Ashraf et al., 2007).

Rheology of concentrated solutions of blends has not been used to investigate the miscibility of the blend components unlike the techniques mentioned above. The aforementioned techniques have limitations of investigation of blend compatibility in concentrated solution. Rheology, by its nature, can be reliably employed for investigating the miscibility of concentrated solutions and melts. In the present work, we report the rheology of the blends of DCOE/PMA, LOE/PMA, DCPEA/PMA and LOPEA/PMA in a highly viscous solution of 8% to predict the morphology and films properties of the blends. A comparative study of these blends is expected to provide an insight into the structural changes that take place at the micron level and can help predict the compatibility, semi-compatibility and even incompatibility of the blends at different compositions in the highly viscous solution phase. Our aim is also to understand how rheological properties can predict blend morphology and its film forming properties.

2. Experimental

Linseed oil (LO) and dehydrated castor oil (DCO) were purchased from M/s Atul Chemicals, Delhi. The oils were dewaxed by keeping them in a refrigerator at 15 °C overnight and filtering before use. Poly(methacrylic acid) (PMAA) was synthesized from methacrylic acid monomer (Aldrich, USA) in the laboratory. Molecular weight of PMAA was determined by viscosity measurement and was found to be 2.3×10^5 Da. Linseed oil epoxy (LOE) and dehydrated castor oil epoxy (DCOE) were prepared after a reported method, which yielded epoxidized oil of epoxy equivalent weight of 260. The dehydrated castor oil polyesteramide (DCPEA) and linseed oil

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polyesteramide (LOPEA) were prepared by a reported method (Ashraf et al., 2005, 2006, 2007a–d).

3. Blending

The blends were prepared by mixing the LOE, DCOE, DCPEA and LOPEA along with PMA in the weight ratios of 80/20, 60/40, 40/60, and 20/80, by taking the requisite amounts of the two components to obtain 100 mL of 8 wt.% solutions of the blend in dimethyl sulfoxide (DMSO; Merck, AR) (Ashraf et al., 2006, 2007a,b,d). All solutions were thoroughly mixed by agitation on a magnetic stirrer for 2 h. Selected samples were kept for over a week. Appearance of turbidity or precipitation was not noticed in any case (Ashraf et al., 2005, 2006, 2007a–d).

4. Characterization

Rheological measurements of blend solutions were carried out on a rheometer, model Brookefield Rheometer RDV III, using a spindle V.L adopter with 25 ml solutions at 5–60 rpm at 30 °C. Viscosity of the blend solutions was measured at temperatures 20, 30, and 40 °C (accuracy 0.05 °C) in a thermostatic bath using an Ubbelhode suspended level viscometer. The ultrasonic velocity of the blend solutions was measured by an ultrasonic interferometer Model MX-20 (Mittal Enterprises, New Delhi). The temperature in the sample cell was maintained at 20, 30, and 40 °C by circulating water from a thermostatic bath through the outer jacket of the sample cell, with a thermal stability of 0.1 °C. The densities of the solutions were measured at the above temperatures by a pycnometer.

5. Results and discussion

5.1. Rheological measurements of blends

The apparent viscosity of 8% solution of DCOE/PMA and LOE/PMA blends at various shear rates is shown in Fig. 1(a) and (b). The figures show that as the shear rate is increased, the apparent viscosity initially increases and becomes constant at 20 s^{-1} indicating that conformation of the polymer blend agglomerate becomes more or less stable and slightly changes with the increasing shear shear rate. This behaviour is also observed for pristine PMA, DCOE and LOE. At higher shear rates, all blend compositions of the system show positive deviation from Newtonian behaviour which can be attributed to the slight incompatibility of the blend components in the solution phase at this concentration. The viscometric studies at 8% of the blends at various compositions also reveal slight incompatibility in the viscosity–composition curves, Fig. 2(a) and (b). We attribute this to some conformational changes in the polymer blend aggregates. The increase in the apparent viscosity at increasing shear rates or stress shows that under increasing shear stress, the layers of the solution are compressed as they move past each other. As a result the molecules come closer and get entangled through electrostatic interaction

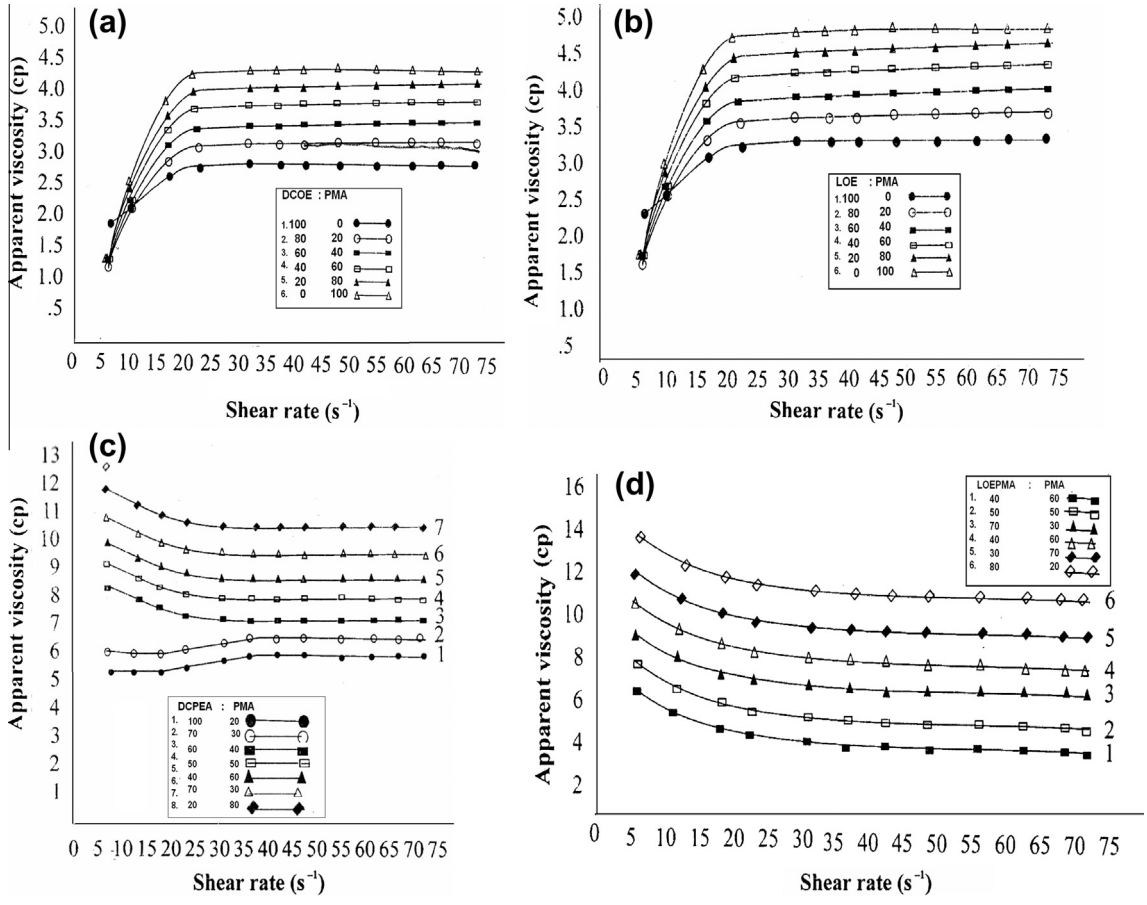

Figure 1 Solution rheology of (a) DCOE/PMA, (b) LOE/PMA, (c) DCPEA/PMA and (D) LOPEA/PMA blends.

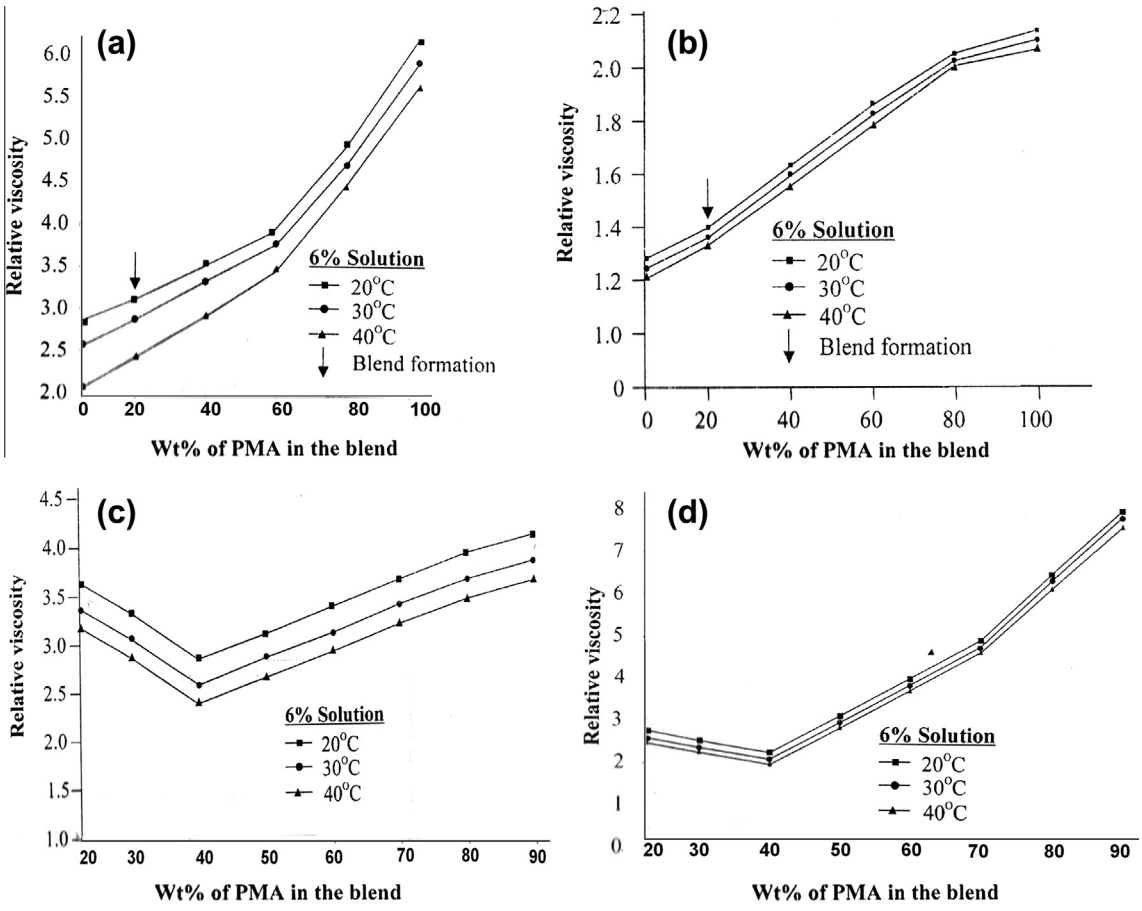

Figure 2 (a) Relative viscosity of (a) DCOE/PMA, (b) LOE/PMA, (c) DCPEA/PMA and (d) LOPEA/PMA blends.

or hydrogen bonding causing increase in the apparent viscosity. For DCPEA/PMA blends, Fig. 1(c), containing 70% PMA the apparent viscosity decreases as the shear rate increases. Beyond 30 s^{-1} shear rate the curve shows a linear behaviour but deviates from the Newtonian behaviour of constant viscosity at various shear rates. Similar behaviour is observed for blends containing 60% PMA and 50% PMA. However an opposite behaviour is observed for the blend containing 30% PMA. In this case, the apparent viscosity increases and becomes constant. In the above composition of the blend, phase inversion occurs which causes a change in the apparent viscosity behaviour from pseudoplastic to a dilatant type fluid. The blend of composition 20% PMA, also shows similar behaviour. The linear portion of the curves from composition containing 70–40% PMA shows slight negative deviation from the Newtonian fluid behaviour. This behaviour along with phase inversion indicates the immiscibility of the components of the blends. The viscosity–composition curve also shows a phase inversion at 40% PMA, Fig. 2(c). The blends of LOPEA/PMA, Fig. 1(d), show pseudo-plastic behaviour with the increase in the shear shear rate which indicates that under increasing shear stress the blend aggregates undergo loosening of the structure and conformational changes which bring about lowering of the viscosity. For the composition LOPEA/PMA containing 30% PMA, the apparent viscosity is higher than the blends containing 40% PMA and 50% PMA and has lower viscosity than blends containing 60% PMA and 80% PMA. This clearly shows phase inversion at 40% PMA indicating incompatibility of the components. The viscosity–composition curve also indicates phase inversion at this composition and corroborates the inference from the rheological measurements, Fig. 2(d).

5.2. Ultrasonic velocity measurements

The ultrasonic velocity reveals slightly nonlinear change at different temperatures exhibiting different slopes as the proportion of PMA in the DCOE/PMA blend increases, Fig. 3(a). Similar behaviour is shown by LOE/PMA blends Fig. 2(b). It is well established for a compatible and miscible blend that the ultrasonic velocity varies linearly with compositions at all concentrations and increases with the increase in temperature i.e. from 20 °C to 40 °C. Since ultrasonic velocity, both for LOE/PMA and DCOE/PMA, deviates from linearity, these blends are therefore partially miscible as was found from rheological measurements.

For DCPEA/PMA, Fig. 3(c), inflections are observed in all the curves at compositions 40% PMA in the blend. The similar nature of nonlinearity is observed at 20 °C, 30 °C and 40 °C. The inflection at 40 wt.% PMA in the blend can be attributed to phase inversion. Similar behaviour is shown by LOPEA/PMA blends, Fig. 3(d). This blend also shows phase inversion at 40% PMA in the blend. Hence the components of the

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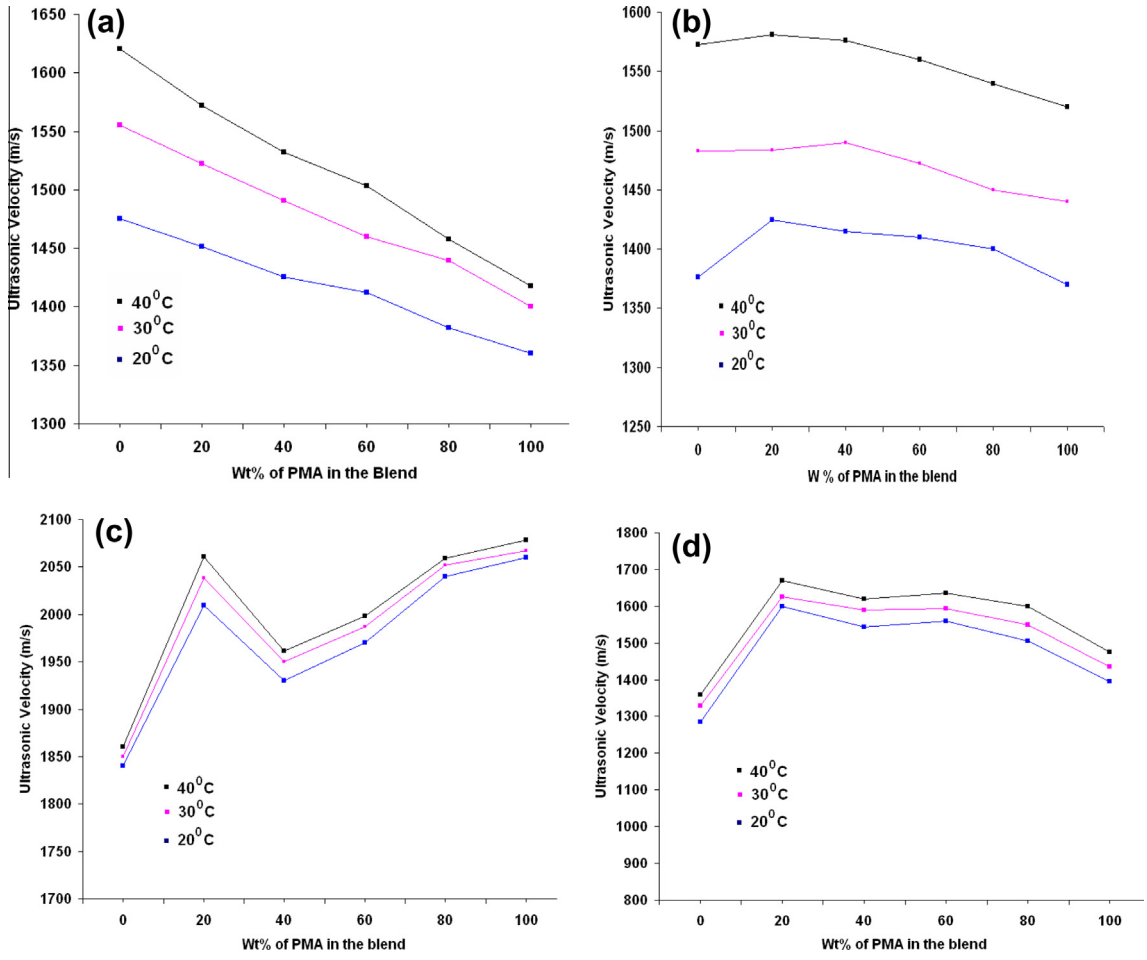

Figure 3 (a) Ultrasonic velocity of (a) DCOE/PMA, (b) LOE/PMA, (c) DCPEA/PMA and (d) LOPEA/PMA blends.

DCPEA/PMA and LOPEA/PMA blends are immiscible. This inference is further corroborated by the observation that the viscosity of these blends at all composition in 8 wt.% solutions shows phase inversion and non linearity at all temperatures. Due to the presence of phase inversion and nonlinearity these blends are immiscible.

5.3. Adiabatic compressibility

Using ultrasound velocity, adiabatic compressibility of the system can be calculated by the following equation (Ashraf et al., 2005, 2006, 2007a–d):

$$\beta = 1/v^2\rho$$

where β is adiabatic compressibility of the medium, v is the velocity of the sound waves and ρ is the density of the medium. Adiabatic compressibility is inversely proportional to the cohesive energy of the polymer molecules. For all the blends, the value of adiabatic compressibility is found to be higher at 20 °C than 40 °C. This indicates that with the increase in the temperature, the interaction between the blend components (via electrostatic or hydrogen bonding) decreases causing loosing of the microstructure.

Fig. 4(a) shows a slight nonlinearity in the adiabatic compressibility of 8 wt% solutions of the blends of different compositions of DCOE/PMA at 20 °C, 30 °C and 40 °C ,which can be correlated to the partial immiscibility of DCOE with PMA as has been inferred previously. The value of adiabatic compressibility is found to be the lowest for the composition 20 wt% PMA in the blend due to the compact structure of the blend resulting from the relatively higher interaction between the components. As the loading of PMA in DCOE increases, the adiabatic compressibility increases. For LOE/PMA blends, Fig. 4(b), variation in the adiabatic compressibility is slightly nonlinear showing slight non miscibility of the components. The adiabatic compressibility is found to be highest for the composition 20 wt% PMA in the blend due to the lower interaction of the blend constituents resulting in loosening of the structure. With the increase in the loading of PMA, the adiabatic compressibility decreases which can be correlated to the increase in interaction between the components.

For DCPEA/PMA, Fig. 4(c), the blend reveals a highly nonlinear behaviour showing maximum adiabatic compressibility at 40% PMA associated with phase inversion indicating the formation of an incompatible blend. Beyond 40 wt.%, the adiabatic compressibility decreases revealing interaction between the blend components. The adiabatic compressibility curves, Fig. 3(d) of LOPEA/PMA blends show multiple

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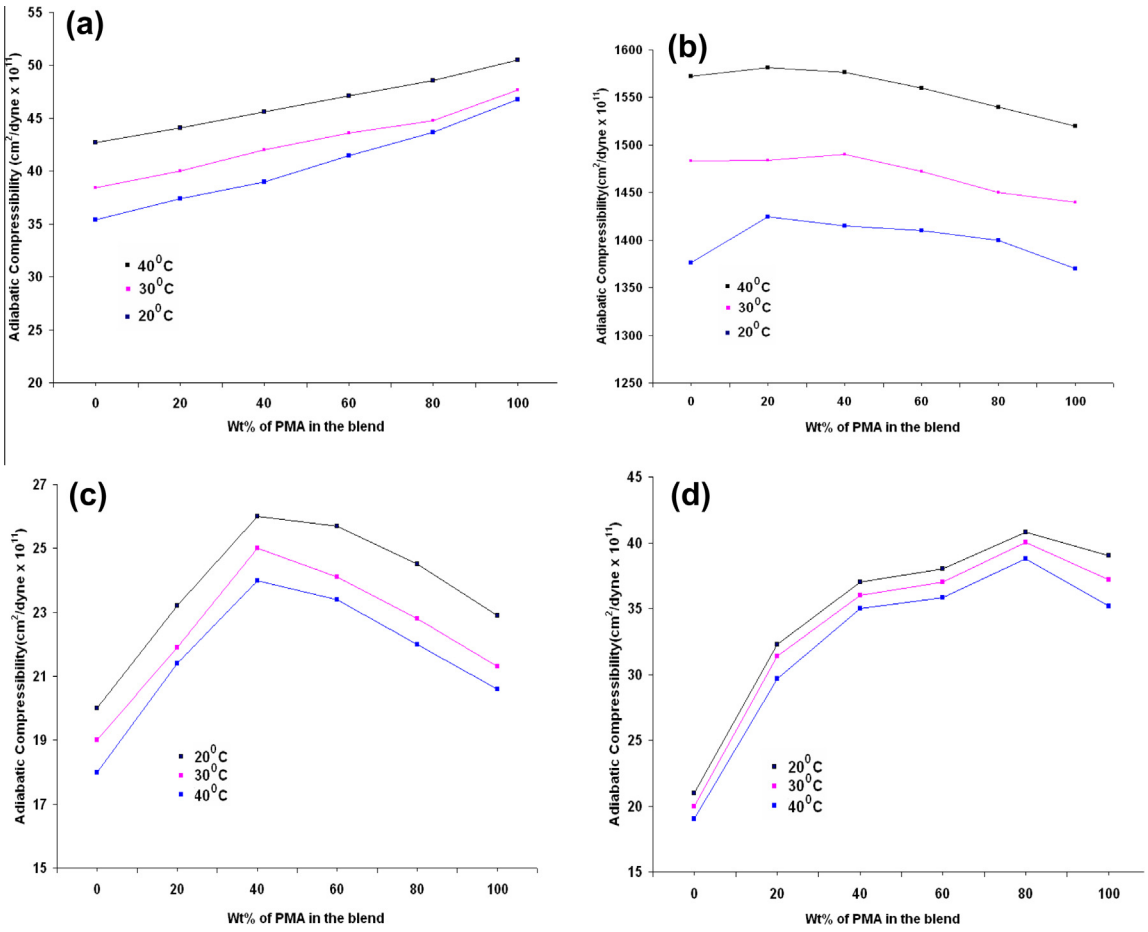

Figure 4 Adiabatic compressibility of (a) DCOE/PMA, (b) LOE/PMA, (c) DCPEA/PMA and (d) LOPEA/PMA.

inflections and nonlinearity, hence immiscibility of the components. As compared to DCPEA/PMA, LOPEA/PMA blends reveal lower-interaction between components with progressive loading of PMA. This can be attributed to the loosening of the blend structure and the decrease in mutual interaction between the components. This observation about the blend structure matches with the inference from the density and the ultrasonic velocity and rheological studies.

5.4. Correlation between rheological behaviour in the solution phase and the film structure in the solid phase

During film formation evaporation of the solvent occurs and volume of the solution decreases. Hence the PMA and DCOE/LOE molecules come close to each other and greater interaction takes place. At higher shear rates, the blends undergo positive deviation from Newtonian behaviour due to partial incompatibility in the solution phase at 8 wt.% concentration. The viscometric studies at various compositions also reveal slight incompatibility in the viscosity–composition curves. As the shear rate or stress increases molecules come close to each other and interact strongly as in case of evaporation for film formation. Hence free standing films are formed in the solid phase.

In case of DCPEA/PMA, the blend containing 30 wt% PMA only yields stable free standing films while higher composition yields brittle and fragile films. This behaviour can be correlated to the rheological behaviour in the solution phase where the viscosity increases with the increasing shear rate. The phase inversion that occurs causes a change in the apparent viscosity behaviour from pseudoplastic to a dilatant type fluid. In case of the blends having high ratio of PMA i.e. 40%, 50%, 70%, stable PMA films are not formed, they remain fluffy. Evaporation occurs with the decrease in apparent viscosity causing loosening of the association between the component molecules which hinder the film formation in these blends. Blends of LOPEA/PMA show pseudo-plastic behaviour which indicates that under increasing shear stress the blend aggregates undergo loosening of the structure and conformational changes that brings about lowering of the viscosity. This loosening of the structure prevents formation of free standing films in the solid phase as molecular association is absent.

6. Conclusion

Rheological measurements show phase inversion, miscibility and partial miscibility in concentrated solutions as explicitly as other techniques used for investigating miscibility of blends in dilute solutions. Rheological measurements also predict the stable and fragile film formation. Only the composition containing 30 wt.% PMA in DCPEA/PMA blends was found to

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yield stable free standing films. Rheological behavior convincingly explains why LOPEA/PMA blends fail to form stable films.

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